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(54) DETERGENT COMPOSITION

(71) We, UNILEVER LIMITED, a company registered under the laws of Great Britain, of Port Sunlight, Birkenhead, Cheshire, England, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a detergent composition that contains an oxygen-liberating bleaching compound, for example sodium perborate and enzymes.

Detergent compositions containing enzymes are mainly used for soaking and pre-washing of laundry at relatively low temperatures, in which use is made of the activity of the enzyme to break down certain persistent stains, e.g. blood, cocoa, casein, etc., before subjecting the laundry to the main wash.

Recently enzymes have been developed that can conveniently be incorporated in bleach-containing heavy-duty detergent compositions such as are normally formulated for use in the main wash, the wash liquor usually being used at a temperature above 50°C. Such compositions usually contain as the bleaching agent a peroxide or an inorganic per compound such as sodium perborate. In view of the proteic nature of the persistent stains subject to attack by enzymes, proteolytic enzymes commercially available such as 'Alcalase', 'Maxatase' and other proteases are generally used. ('Alcalase' and 'Maxatase' are Registered Trade Marks).

It has been found however that enzyme-containing heavy-duty detergent compositions suffer from certain drawbacks. Whereas the enzymes in pre-wash and soaking formulations are relatively stable, the bleaching agent present in heavy-duty detergent formulations adversely affects the stability of the enzymes. The activity of the enzyme tends to decrease during production of the detergent powder and also on storage; the rate of decrease in activity varies according to time, temperature and relative humidity, although the influence of the latter can be eliminated to a large extent by storing the powder in special waterproof packs, e.g. in wax-laminated cartons. But in order to secure proper enzymatic action an excess of enzymes must normally be incorporated to allow for loss of activity.

An additional and serious drawback that has now been appreciated is that in removing certain important types of proteic stains, particularly blood stains, the enzyme-containing heavy-duty compositions do not show satisfactory advantages over conventional heavy-duty compositions without enzymes. Whereas blood stains can be effectively removed from fabrics by soaking/pre-washing treatment with a conventional enzyme-containing formulation followed by a heavy-duty main wash, they cannot be satisfactorily removed by washing with a conventional heavy-duty detergent composition nor by washing with such a composition in which enzymes have been incorporated; prior treatment with an enzyme-containing soaking/pre-washing product is necessary. In this respect the incorporation of enzymes in a heavy-duty composition is more or less wasted.

Apparently the presence of per compounds in the wash liquor inhibits the effectiveness of enzymes on proteic-type stains. It is believed that even at temperatures of 30°C to 50°C, at which the enzymes are normally effective, the presence of active oxygen from the per compounds affects the nature of the protein in stains such as those discussed above in such a way that they cannot be completely removed from the fabric by enzyme activity even if a subsequent boiling step is used.

The present invention provides a detergent composition, particularly a heavy-duty detergent composition, that contains an oxygen liberating bleaching agent as well as enzymes, and in which the above disadvantages are reduced.

The invention provides a heavy-duty detergent composition containing an oxygen liberating bleaching agent and enzymes, in which the bleaching agent is coated or encapsulated with a material that dissolves, disperses or melts in wash liquor above 50°C, preferably above 60°C, and below 85°C, preferably below 70°C. The coating or encapsulating material cannot release the bleaching agent in the wash liquor at a temperature less than 50°C. The simplest way to encapsulate the bleaching agent is by packing it in small sachets, but particle-coating is to be preferred since a much better distribution of the bleaching agent during the washing process can be attained. The coating or encapsulating material can be a water-insoluble and indifferent material or a detergent auxiliary material that has a melting point not less than 50°C and not more than 85°C, preferably 70°C. Alternatively the coating or encapsulating material can be a material that dissolves or disperses, not necessarily melts, in the wash liquor at a temperature not less than 50°C and not more than 85°C, preferably 70°C. Preferably the coating or encapsulating material has a melting point or dispersing point between 60°—70°C.

Examples of such materials are fatty acids, such as palmitic acid, stearic acid, arachidic acid; paraffins; waxes; and mono-, di or triglycerides of single or mixed fatty acids.

The enzymes will be free, that is they are free to contact wash liquor below 50°C. They can, in a preferred form of the invention, also be coated or encapsulated. The coating or encapsulating material used for the enzymes is, as distinct from that used for the bleaching agent, a water-soluble or water-dispersible material that is capable of releasing the enzymes in the washing liquor at a temperature lower than 50°C, preferably lower than 40°C. Examples of such materials include sugar, nonionic surface-active agents, polyvinylalcohol, and sodium carboxymethylcellulose, the latter material commonly being used in detergent compositions as an anti-redeposition agent.

Any suitable technique for particle coating and encapsulating substances can be used for coating sodium perborate or other per compound bleach or optionally enzymes to be incorporated in the detergent composition according to the invention. Suitable techniques are described in the literature, for example in U.S. patent specifications Nos. 3,112,274 and 3,161,602 and in French patent specification No. 999,775.

The invention is not restricted to a detergent composition containing solid per compound bleaching agents such as perborate, but is also applicable to a composition containing liquid peroxide compounds, such as hydrogen peroxide, as the bleaching agent. In this case the liquid bleaching compound is incorporated in the detergent composition in an encapsulated form.

The detergent composition according to the invention can further be of the high, medium or low sudsing type depending on its purpose of use. It may be of the anionic, nonionic or mixed active type containing the usual constituents for heavy-duty performance. As such can in the first place be mentioned detergent active substances, e.g. alkylarylsulphonates; alkane sulphonates; alkene sulphonates; alkyl sulphates, soap; and alkylene oxide adducts of alcohols or alkylphenols. Various combinations of detergent active substances can be used in the enzymatic heavy-duty detergent compositions according to the invention. By suitable combinations of the various anionic detergents with the nonionic substances the detergency and foaming characteristics of the compositions according to the invention can be adjusted properly. Medium to low foaming compositions may e.g. be obtained through combinations of detergent active sulphonates or sulphates with soap and nonionic active substances of the alkylene oxide adducts type. Secondly, there may also be included organic and/or inorganic builder materials, e.g. sodium tripolyphosphate, and further such adjuvants as sodium silicate, sodium sulphate, soil suspending agents, and optical bleaches. Other additives, such as perfumes, and colouring substances, can be added if desired.

The relative amounts of the above-mentioned ingredients in the composition are not very critical. Any heavy-duty detergent bleach formulation known in the art can be used as a basis for the composition according to the invention. Such formulations contain by weight generally 1—30% detergent active substances, 10—50% organic and/or inorganic builders, 10—30% per compound bleaching agent and up to 30% other adjuvants and additives.

The amount of enzymes incorporated in such compositions is dependent upon their activity. In general the amount is such that the activity of the enzymes in the final product lies between 4—20 Anson units per kg final product, which corresponds with approximately 0.5—20% by weight of enzyme in the final product.

An Anson unit is the amount of proteolytic enzyme which degrades haemoglobin under the standard conditions as described by M. L. Anson in "Journal of General Physiology", Vol. 22 (1938), p.79, with such an initial velocity that per minute an amount of degradation products is obtained which are not precipitable by trichloroacetic acid, which produces the same colour intensity as 1 milliequivalent tyrosine with the phenol reagent.

The advantage of the detergent compositions according to the invention is that their washing performance is that of a combined action of

biological pre-washing and main wash, thus simplifying the general washing operation, since by using the detergent composition according to the invention a pre-washing and/or soaking formulation need not be used.

Note that the detergent composition according to the invention can be used for both pre-washing and/or soaking as well as for the main wash.

In the following Example the invention is further illustrated.

EXAMPLE

Washing experiments were carried out with the fololwing detergent compositions (parts and percentages are by weight):

	A	B_1—B_4	C_1—C_7	D_1—D_2
Sodium dodecyl benzene sulphonate	20%	20%	20%	20%
Sodium tripolyphosphate	40%	40%	40%	40%
Sodium carboxymethylcellulose[1]	1%	1%	1%	1%
Sodium sulphate	25%	5%	5%	25%
Waterglass	5%	5%	5%	5%
Water	9%	9%	8%	8%
Sodium perborate	—	20%	20%	—
Enzyme	—	—	0.8—1%	0.8—1%

[1]Present as an anti-redeposition agent (not as a coating or encapsulating material).

Compositions B_1, C_1 and C_2 contained free sodium perborate.

Compositions B_2, C_3 and C_5 contained coated sodium perborate which was released at about 50°C.

Compositions B_3, C_4 and C_6 contained coated sodium perborate which was released at about 60°C.

Compositions B_4 and C_7 contained coated sodium perborate which was released at about 70°C.

The coating of the sodium perborate used in compositions B_2 to B_4, and C_3 to C_7 was accomplished by a fluidised bed technique as described in US patent specification No. 3,161,602. In this process 400 parts of sodium perborate were coated with 265 parts of coating material. The coating material for sodium perborate to be released at about 50°C was an 80/20 mixture of hardened palm and palm kernel oils. The coating material for sodium perborate to be released at about 60°C was a mixture of 25% paraffin wax, 50% ozokerite and 25% carnauba wax, and the coating material for sodium perborate to be released at about 70°C was behenic acid monoglyceride.

The effect of active oxygen from sodium perborate released at various stages in the washing process was determined using the above basic compositions in a Tergotometer test. Blood-stained test clothes were used. The following test conditions were:

Water	15°G.H.
Machine adjustment	75 strokes/min.
Cloth/liquor ratio	1:50
Detergent concentration	5 g/l

The results of the washing efficiencies of the above compositions obtained from reflection measurements of the test cloths using the Elrephotometer are shown in the following table:

	30 min. to 60°C 10 min. at 60°C			55 min. to 95°C. 10 min. at 95°C.	
	without enzyme	'Alcalase' 40 mg/l	'Maxatase' 45 mg/l	without enzyme	'Alcalase' 40 mg/l
without sodium perborate	(A) 37	(D_1) 49	(D_2) 48	(A) 56	(D_1) 58
sodium perborate present at beginning 100 mg/l active oxygen	(B_1) 9	(C_1) 15	(C_2) 12	(B_1) 38	(C_1) 47
sodium perborate released in washing liquor at about 50°	39(B_2)	56(C_3)	58(C_5)	64(B_2)	74(C_3)
60°	42(B_3)	58(C_4)	57(C_6)	65(B_3)	74(C_4)
70°	—	—	—	64(B_4)	74(C_7)

Similar results were obtained using the above composition with hydrogen peroxide in place of sodium perborate.

These results show that the removal of blood stains is incomplete in the presence of active oxygen from either sodium perborate or H_2O_2. The addition of proteolytic enzymes does not lead to the normal level of stain removal by enzymes. The superior effect of compositions with coated or encapsulated perborate, released at a temperature of 50°—70°C in the washing liquor according to the invention over conventional compositions is evidently shown.

WHAT WE CLAIM IS:—

1. A detergent composition containing both an oxygen liberating bleaching agent that is coated or encapsulated with material that dissolves, disperses or melts in wash liquor above 50°C and below 85°C, and enzymes that are free, or coated or encapsulated with a material that disssolves, disperses or melts in wash liquor below 50°C.

2. A detergent composition as claimed in Claim 1, in which the bleaching agent is sodium perborate.

3. A detergent composition as claimed in Claim 1 or 2, in which the bleaching agent is coated or encapsulated with a material that dissolves, disperses or melts in wash liquor above 60°C and below 70°C.

4. A detergent composition as claimed in Claim 1, substantially as described herein and with particular reference to the Example.

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